

This Page Is Inserted by IFW Operations
and is not a part of the Official Record

BEST AVAILABLE IMAGES

Defective images within this document are accurate representations of the original documents submitted by the applicant.

Defects in the images may include (but are not limited to):

- BLACK BORDERS
- TEXT CUT OFF AT TOP, BOTTOM OR SIDES
- FADED TEXT
- ILLEGIBLE TEXT
- SKEWED/SLANTED IMAGES
- COLORED PHOTOS
- BLACK OR VERY BLACK AND WHITE DARK PHOTOS
- GRAY SCALE DOCUMENTS

IMAGES ARE BEST AVAILABLE COPY.

**As rescanning documents *will not* correct images,
please do not report the images to the
Image Problem Mailbox.**



Europäisches Patentamt
European Patent Office
Office européen des brevets

Publication number:

0 403 461
A1

12

EUROPEAN PATENT APPLICATION

21 Application number: 90850236.2

51 Int. Cl. 5: C23C 30/00, C23C 16/40

22 Date of filing: 14.06.90

30 Priority: 16.06.89 SE 8902179

43 Date of publication of application:
19.12.90 Bulletin 90/51

64 Designated Contracting States:
AT CH DE FR GB IT LI NL SE

71 Applicant: SANDVIK AKTIEBOLAG
S-811 81 Sandviken 1(SE)

72 Inventor: Chatfield, Christopher
Vedstigen 33
S-147 52 Tumba(SE)

Inventor: Lindström, Jan
Hökmossevägen 28
S-126 38 Hägersten(SE)
Inventor: Sjöstrand, Mats
Stavangergatan 42
S-164 33 Kista(SE)
Inventor: Collin, Marianne
Kanslersvägen 28
S-122 36 Enskede(SE)

74 Representative: Östlund, Alf Olof Anders et al
Sandvik AB Patent Department
S-811 81 Sandviken(SE)

54 Coated cutting insert.

57 The present invention relates to a body coated with at least one double layer Al_2O_3 -TiC. Because the Al_2O_3 -layer in contact with the TiC-layer consists of kappa- Al_2O_3 or theta- Al_2O_3 an improved adherence has been obtained.

A further improvement of the properties is obtained if the body after the coating is heat treated for 0.3-10 hours at 900-1100 °C in protecting gas atmosphere at which initially nucleated kappa- or theta- Al_2O_3 is transformed to fine-grained alpha- Al_2O_3 .

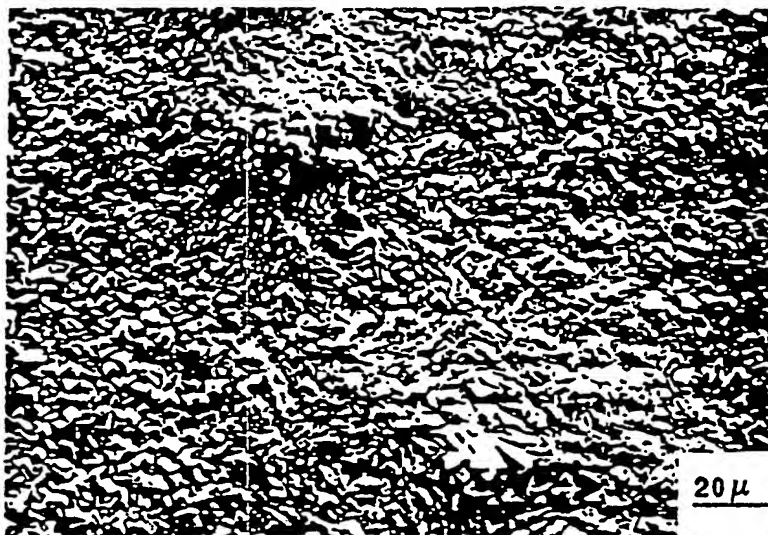


FIG 2

EP 0 403 461 A1

Coated cutting insert

The present invention relates to a coated cutting insert for chipforming machining.

Chemical Vapor Deposition of alumina on cutting tools has been an industrial praxis for more than 15 years. The wear properties of Al_2O_3 as well as of TiC and TiN have been discussed extensively in the literature.

The CVD technique has also been used to produce coatings of other metal oxides, carbides and nitrides with the metal either selected from the transition metals of the groups IVB, VB and VIB of the Periodic Table or from silicon, boron and aluminium. Many of these compounds have found practical applications as wear resistant or protective coatings, but few have received as much attention as TiC, TiN and Al_2O_3 .

Initially coated tools were intended for turning applications, but today tools designed for milling as well as drilling applications, are coated. Improvements of the bonding to the substrate and between different coating materials have resulted in a plurality of coating combinations with double-, triple- or multi-layer structures.

The reaction mechanisms occurring during the CVD of Al_2O_3 have been analysed, but little has been mentioned about the stability and microstructure of the deposited Al_2O_3 phases and how the formation of these phases depends on the deposition process.

Al_2O_3 crystallizes in several different phases of which the alpha-structure (corundum) is the thermodynamically stable phase at typical deposition temperatures. The metastable kappa-phase is the second most commonly occurring modification in CVD- Al_2O_3 . Other infrequently occurring types are theta-, gamma- and delta- Al_2O_3 .

In commercial tools Al_2O_3 is always applied on TiC-coated cemented carbide (see e.g. SE 357 984) and therefore the interface reactions on the TiC-surface are of particular importance. (With TiC-layer is also understood those layers having the formula $\text{TiC}_x\text{N}_y\text{O}_z$ in which C in TiC is completely or partly substituted by oxygen and/or nitrogen. In the system $\text{TiC}_x\text{N}_y\text{O}_z$ there is 100 % miscibility. There can be one or more layers of this kind. Similar relationships also exist within other systems e.g. Zr-C-N-O.)

The purpose of the present invention has been to obtain such an Al_2O_3 -layer with the correct crystallography, microstructure and morphology and under nucleation conditions such that the desired Al_2O_3 -phases will be stabilized.

A typical surface structure of a CVD- Al_2O_3 coating contains coarse-grained islands of alpha- Al_2O_3 , the first Al_2O_3 phase to nucleate, surrounded by much more fine-grained kappa- Al_2O_3 -areas. When greater amounts of such alpha- Al_2O_3 exist the individual islands join together. The ratio coarse-grained/fine-grained areas can vary over broad intervals.

Also the alpha/kappa ratio measured by X-ray diffraction will vary over a wide range. A higher ratio is obtained at long coating times and after further heat treatment. After about 3 hours' heat treatment at 1000 °C essentially all the thermodynamically metastable kappa- Al_2O_3 is transformed to stable alpha- Al_2O_3 . It is important to note that the transformation kappa → alpha takes place without any great changes in surface morphology. The alpha- Al_2O_3 formed from kappa is fine-grained.

The kinetics behind the phase transformation metastable kappa- Al_2O_3 to stable alpha- Al_2O_3 is not clear. It should be noted, however, that only small re-arrangements of the close-packed oxygen layers, that are common to both structures, are needed to convert kappa- to alpha- Al_2O_3 .

In the Swedish patent No. 406090 a method of making kappa- Al_2O_3 has been proposed being based essentially on the fact that an addition of TiCl_4 to the gas mixture results in kappa- Al_2O_3 formation. Any kappa-phase, formed under these conditions, having an epitaxial relationship with the layer below a thick Al_2O_3 -layer has not been formed, however. (A thick Al_2O_3 -layer is more than 2 μm Al_2O_3).

The microstructure of an alpha- Al_2O_3 coating initially nucleated as alpha- Al_2O_3 is characterized by a grain size of about 0.5-5 μm , preferably 0.5-2 μm , and the presence of pores. Contrary to this a kappa- Al_2O_3 coating is essentially pore-free and has a much smaller grain size of about 0.05-2 μm , preferably 0.05-1 μm , usually about 0.2-0.5 μm .

It has now been found that poor adhesion between the Al_2O_3 -layer and the underlying TiC-layer is obtained if the Al_2O_3 in direct contact with the TiC-layer has the alpha- Al_2O_3 crystal structure at the time when it is nucleated. In such a case considerable porosity exists between the two layers. If kappa- or theta- Al_2O_3 on the other hand is in a direct contact with the TiC-layer the transition is pore-free and good adhesion is obtained. In said latter case a direct lattice relationship exists between the orientations of the Al_2O_3 - and the TiC-layers, i.e. the Al_2O_3 -layer grows epitaxially. The following relationships exist between TiC / kappa Al_2O_3 :

(1 $\bar{1}1$) TiC // (0001) κ -Al₂O₃

[110] TiC // [10 $\bar{1}$ 0] κ -Al₂O₃

and between TiC / θ -Al₂O₃:

(111) TiC // (310) θ -Al₂O₃

5 [1 $\bar{1}$ 0] TiC // [001] θ -Al₂O₃

Both these can be interpreted as indicating that close-packed atom planes in the Al₂O₃- and TiC-phases are in contact and thus the adhesion across the interface between Al₂O₃ and TiC will be maximized. Similar epitaxial relationships should also exist between Al₂O₃ and metal systems related with TiC e.g. ZrC and for other carbides, carbonitrides, oxynitrides, oxycarbides, oxycarbonitrides and nitrides of metals in the groups IVB, VB and VIB of the Periodic Table and for B, Al and Si and should maximize adhesion between the phases on either side of the interface.

The process conditions governing the first nucleation event are thus of great importance. The oxidation state of the TiC-surface is decisive for the kind of nuclei which are to be formed. If the TiC-surface is (intentionally) oxidized only α -Al₂O₃ is formed. Simple calculations show that the presence of water in H₂ carrier gas has a dramatic effect on the oxidation state. Already at 5 ppm water in H₂ at 1000 °C and 50 mbar the TiC surface oxidizes to Ti₂O₃. At higher water contents (20-30 ppm) Ti₃O₅ is formed. It should be observed that the formation of titanium oxide (Ti₂O₃, Ti₃O₅) involves a volume increase of 25-30 %. Also other oxygen containing compounds than water in the feed-gas can cause oxidation.

The water gas concentration in the reactor during Al₂O₃ coating at typical conditions for good adhesion is very small and all water is used during the hydrolysis reaction with AlCl₃. For a typical reactor the water content is 0.01-0.1 ppm. The water concentration varies, however, greatly during the nucleation event and can locally reach 1000-2000ppm. It is thus possible to oxidize the TiC surface during the Al₂O₃ nucleation stage.

Another contribution to the oxidation of the TiC-surface comes from the heterogenous decomposition of CO₂, in which surface adsorbed mono-atomic oxygen can oxidize the TiC-surface.

It is surprising that such low-oxidizing conditions would be necessary to obtain a well-adherent oxide coating (Al₂O₃). Prior art even recommends the use of oxidized surfaces to form well-adherent dense Al₂O₃-coatings. (see e.g. U.S. Pats. No. 3,736,107 , 3,837,896 , 4,018,631 or 4,608,098).

It has thus been found that no well-defined lattice-orientation relationship exists between TiC and α -Al₂O₃, which has been nucleated on TiC from gas phase. Instead the TiC-Al₂O₃ interface contains a great amount of porosity. It is therefore very probable that the nucleation of α -Al₂O₃ does not take place on TiC but on a thin oxide film of e.g. Ti₂O₃, Ti₃O₅ or TiO₂ what thus makes the formation of an epitaxial relationship with the underlying TiC-surface impossible. However, because there is no trace of any intermediate layer of Ti₂O₃, Ti₃O₅ or TiO₂ in the final product it must be assumed that a transformation to TiO, TiCO or TiC has happened during the relatively extended coating period. The volume contraction (25-30%) which accompanies the phase transformation Ti₃O₅ or Ti₂O₃ to TiO would explain the observed interfacial porosity.

Contrary to this, κ -Al₂O₃ or θ -Al₂O₃ is nucleated directly on non-oxidized or relatively weakly oxidized (up to highest Ti₂O₃) TiC-surfaces, which results in an epitaxial relationship between the TiC- and the Al₂O₃-layers and, as then, no reduction of Ti₂O₃ etc to TiO occurs, thus in the absence of porosity.

The α -Al₂O₃ is, as mentioned, the stable structure and has a higher density than κ -Al₂O₃. If, during the nucleation event κ -Al₂O₃ is formed then the resulting layer will have a more fine-grained and uniform structure than, in particular, a mixture of κ - and α -Al₂O₃. If only or almost only α -Al₂O₃ is obtained it takes place in connection with the reduction of higher titanium oxides (e.g. TiO₂, Ti₃O₅) and porosity will be formed.

Fig. 1 shows a "prior art" Al₂O₃-surface consisting of initially nucleated α - (coarse-grained) and κ - (fine-grained) structure.

Fig. 2 shows the same microstructural feature, but after 4 hours' heat treatment, by which a microstructure of α -Al₂O₃ of fine-grained type has been obtained (according to the invention) mixed with initially formed α -Al₂O₃ ("prior art" structure).

According to the invention there is thus now available a body such as e.g. a cutting insert for chipforming machining coated with at least one layer of Al₂O₃ + TiC in which the Al₂O₃-layer is in epitaxial contact with adjacent TiC-layer and consists of κ - or θ -Al₂O₃. In general the Al₂O₃-layer consists of at least 90 %, preferably at least 98 % α -Al₂O₃ which has been initially nucleated as κ - or θ -Al₂O₃ and which has been obtained by a subsequent heat treatment. By this measure a dense and wear resistant α -Al₂O₃ is obtained which is fine-grained and has a good bond to the underlying TiC-, TiN- or TiO-layer. The fine grain size and the good bond are caused by the excellent nucleation properties of the initially nucleated κ -Al₂O₃-layer. In said respect the invention can be described as α -Al₂O₃ with

kappa-Al₂O₃-morphology. That is, the occurrence of alpha-Al₂O₃ can only be verified by X-ray diffraction or similar methods.

The invention also relates to a method for obtaining Al₂O₃-layers with good adherence to the substrate (including the TiC, TiN etc interlayer). By said method the coating shall be performed so that oxidization of the surface of the TiC-layer is avoided at the transition to the Al₂O₃-coating process by keeping the water vapor concentration at the nucleation below 5 ppm, preferably below 0.5 ppm. In this context it should be noted that the interlayer must have a thickness and such properties that metals (e.g. Co) catalyzing the CO₂ decomposition to oxygen and CO cannot penetrate the interlayer and cause excessive oxidation of the surface on which Al₂O₃ is to be nucleated. The coated body can then alternatively be heat treated in 0.3-10, preferably 1-4 hours, at a temperature of 900-1000 °C preferably in a protective gas atmosphere.

With double layer is also meant known layers of current multilayer inner as well as outer layers. Also when e.g. TiC or TiN is deposited on Al₂O₃ the invention can be applied.

15 Example 1

Cutting inserts were coated under the same conditions as in Example 1 in SE 357 984 by which a 3 µm thick layer was obtained by suitably sparse packing. The water concentration was kept to such a low level before and during the Al₂O₃- nucleation that mainly kappa-Al₂O₃ was nucleated in contact with TiC, cutting insert A.

The cutting inserts were then tested with respect to edge line flaking with the result given below:

(The flaking test was performed as a facing operation of a low carbon steel test piece with intermittent cuts obtained by preformed slits cut into the test piece. Since low carbon steels vary in composition and other properties the configuration of the slits and cutting data must be adjusted by performing preliminary tests enabling final best conditions to be obtained. The result of the cutting test is expressed as the ratio of flaking length of the edge line and the total edge line in the cutting operation.)

Test	% alpha-Al ₂ O ₃	flaking
A	15	70 (acc. to the inv.)
B	90	90 (known techn.)

Testing of the wear resistance showed that the variant B, in addition, had inferior face wear resistance and shorter life.

40 Example 2

Cutting inserts coated under the same conditions as in Example 1 and in which the coating thus consisted essentially of about 3 µm kappa-Al₂O₃ were heat treated at 1020 °C in a hydrogen gas atmosphere and the kappa-phase was succesively transformed to alpha-phase.

The inserts were then tested with respect to edge line flaking with results below:

Test	Heat treatment time, h	% alpha-Al ₂ O ₃	flaking
C	8	100	65
D	2	35	50

Testing of the wear resistance showed that the variant D had inferior face wear resistance and the shortest life of the inserts C and D.

55 Example 3

Cutting inserts were coated in accordance with Example 1 in SE 357 984 at which 1 μm Al_2O_3 -layer was obtained by a dense packing of inserts and supporting details. The coated inserts had a high carbon content so that about 6 μm thick TiC-layer was formed. Inserts were taken out from different parts of the coating charge. One group of inserts had kappa- Al_2O_3 in contact with the TiC-layer. These inserts showed in an intermittent turning test no tendency for the Al_2O_3 -layers to "flake" from the TiC-layer. Another group of inserts with almost only alpha- Al_2O_3 in contact with TiC flaked to about 45% of the surface exposed to the chip.

10 Claims

1. Body coated with at least one double layer of Al_2O_3 and TiC or related carbides, nitrides, carbonitrides or oxycarbonitrides characterized in, that the Al_2O_3 -layer in contact with said carbide-, nitride-, carbonitride- or oxycarbonitride-layer consists of epitaxial kappa- Al_2O_3 or theta- Al_2O_3 .
2. Body according to claim 1 characterized in that the following phase relationship exists between TiC/kappa- Al_2O_3 :
 $(1\ \bar{1}\ 1)\ \text{TiC} \parallel (0001)\ \text{kappa-}\text{Al}_2\text{O}_3$
 $[110]\ \text{TiC} \parallel [10\ \bar{1}\ 0]\ \text{kappa-}\text{Al}_2\text{O}_3$
3. Body according to claim 1 characterized in, that the following phase relationship exists between TiC/theta- Al_2O_3 :
 $(111)\ \text{TiC} \parallel (310)\ \text{theta-}\text{Al}_2\text{O}_3$
 $[1\ \bar{1}\ 0]\ \text{TiC} \parallel [001]\ \text{theta-}\text{Al}_2\text{O}_3$
4. Body according to any of the preceding claims characterized in, that the Al_2O_3 -layer consists of alpha- Al_2O_3 with a grain size of $< 1\ \mu\text{m}$, at which alpha- Al_2O_3 has been formed from initially nucleated kappa- or theta- Al_2O_3 .
5. Method of coating a body with Al_2O_3 characterized in, that the content of water vapour at the nucleation event is $< 30\ \text{ppm}$, preferably $< 5\ \text{ppm}$.
6. Method according to claim 5 characterized in, that the body after the coating is heat treated for 0.3-10 hours at $900\text{-}1100\ ^\circ\text{C}$ in protecting gas atmosphere.

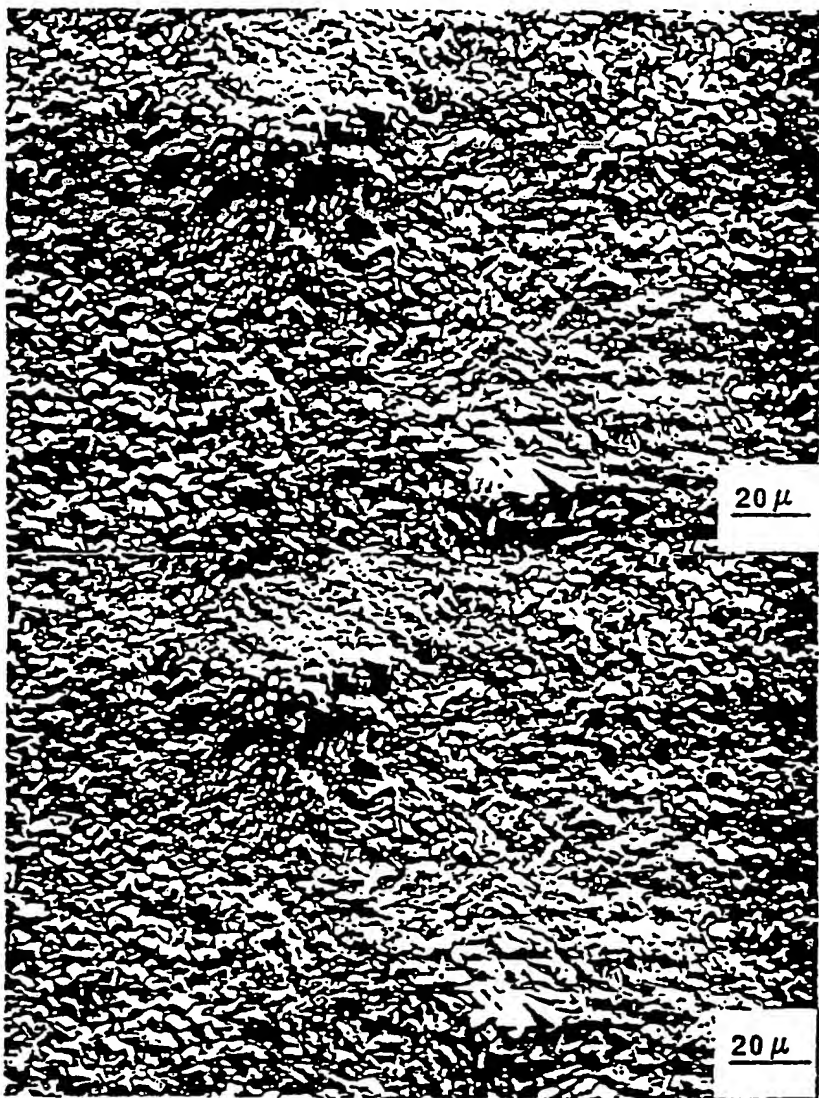


FIG 1

FIG 2



European Patent
Office

EUROPEAN SEARCH REPORT

Application Number

EP 90 85 0236

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. CL.5)
X	EP-A-0 045 291 (SANDVIK) * claims 1,5 * ---	1	C 23 C 30/00 C 23 C 16/40
X	EP-A-0 032 887 (SANDVIK) * example 1 * ---	1,5	
P,X	PATENT ABSTRACTS OF JAPAN vol. 13, no. 290 (C-614)(3638), 5 July 1989; & JP-A-183662 (KYOCERO CORPORATION) 29.03.1989 ---	1	
X	US-A-4 180 400 (K.K.H. SMITH et al.) * claim 1 *; & SE-B-406090 (cat. D) ---	1	
A	EP-A-0 083 842 (GENERAL ELECTRIC) & US-A-4608098 (cat. D) ---		
D,A	US-A-4 018 631 (T.E. HALE) ---		
D,A	US-A-3 837 896 (J.N. LINDSTROEM et al.) & SE-B-357984 ---		
D,A	US-A-3 736 107 (T.E. HALE) -----		
The present search report has been drawn up for all claims			
Place of search BERLIN		Date of completion of the search 04-09-1990	Examiner KESTEN W.G.
CATEGORY OF CITED DOCUMENTS X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document		T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons ----- & : member of the same patent family, corresponding document	